

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-138669

(43)Date of publication of application : 31.05.1996

(51)Int.CI. H01M 4/58 H01M 4/02 H01M 10/40

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(54) CATHODE ELECTROACTIVE MATERIAL, THE MANUFACTURING PROCESS, AND NON-AQUEOUS SOLVENT SECONDARY BATTERY USING THE MATERIAL

(57)Abstract:

PURPOSE: To provide a high capacity and an excellent charge - discharge cycle performance by using a compound having a specified composition with a chemical formula; $\text{Li}_{1-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_2$ as a positive active material.

CONSTITUTION:

(1) A compound having a chemical formula $\text{Li}_{1-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_2$ is used as a positive electroactive material, wherein A stands for alkali or alkaline earth metal elements, B for at least one sort of transition metal elements, $0 < x \leq 0.10$, $0 < y \leq 0.30$ mole ratio. When B consists of two or more kinds of transition metal elements, y means the total mole ratio of the transition metal elements. And when $y=0$, A contains at least an alkaline earth metal.

(2) A starting raw material containing lithium or A is added to a starting raw material containing nickel or B in the stoichiometric ratio (of the former to the latter) from 1.05 to 1.25, the raw materials are fired in oxygen atmosphere, and non-reacted alkali components are removed. As a result, the amount of an alkali metal with which lithium is substituted can be lessened and thus the decrease of the initial capacity is suppressed.

AND

CLAIMS

[Claim(s)]

[Claim 1] The electroactive material using a compound expressed with chemical formula; $\text{Li}_{1-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_2$, wherein A is alkali or alkaline-earth metal element, and B is at least one sort of transition-metal elements. $0 < x \leq 0.10$, $0 < y \leq 0.30$. When B consists of two or more kinds of transition metal elements, y means the total mole ratio of the transition metal elements. And when $y=0$, A contains at least an alkaline earth metal.

[Claim 2] The manufacturing method of the positive electroactive material according to Claim 1, wherein a starting raw material containing lithium or A is added to a starting raw material containing nickel or B in the stoichiometric ratio of 1.05 to 1.25 to the latter, and the non-reacted alkaline components are removed after the raw materials are fired in oxygen atmosphere.

[Claim 3] The manufacturing method of the positive electroactive material according to Claim 2, wherein the removal of the said alkaline components is carried out by washing with water.

[Claim 4] The non-aqueous-solvent rechargeable battery characterized by using a positive electroactive material according to Claim 1.

[Claim 5] The non-aqueous-solvent rechargeable battery according to Claim 4 characterized by using the positive electroactive material manufactured by the method according to Claim 2.

[Claim 6] The non-aqueous-solvent rechargeable battery according to Claim 4 or 5 characterized by using a carbonaceous material for a negative electroactive material.

[Claim 7] The non-aqueous solvent rechargeable battery given in any one claim out of the Claims 4-6 to which this carbonaceous material is characterized by carbon fiber.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0012] [Purpose of this invention]

To offer a cathode active material which has high capacity and good cycleability, and secondary battery using this cathode material.

[0028]

[Example]

[Table 1]

表1. 実施例の仕込み組成と定量分析組成

	上段：仕込み組成／下段：定量分析組成
実施例1.	$\text{Li}_{1.23}\text{Ba}_{0.025}\text{Ni}_{1.00}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.021}\text{Ni}_{1.0}\text{O}_2$
実施例2.	$\text{Li}_{1.23}\text{Sr}_{0.025}\text{Ni}_{1.00}\text{O}_2$ $\text{Li}_{0.98}\text{Sr}_{0.021}\text{Ni}_{1.0}\text{O}_2$
実施例3.	$\text{Li}_{1.07}\text{K}_{0.033}\text{Ni}_{0.900}\text{Mn}_{0.100}\text{O}_2$ $\text{Li}_{0.97}\text{K}_{0.030}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
実施例4.	$\text{Li}_{1.07}\text{Na}_{0.036}\text{Ni}_{0.90}\text{Mn}_{0.100}\text{O}_2$ $\text{Li}_{0.97}\text{Na}_{0.031}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
実施例5.	$\text{Li}_{1.08}\text{Ba}_{0.022}\text{Ni}_{0.900}\text{Mn}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.020}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
実施例6.	$\text{Li}_{1.05}\text{Ba}_{0.055}\text{Ni}_{0.900}\text{Mn}_{0.100}\text{O}_2$ $\text{Li}_{0.95}\text{Ba}_{0.051}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
実施例7.	$\text{Li}_{0.990}\text{Ba}_{0.11}\text{Ni}_{0.900}\text{Mn}_{0.100}\text{O}_2$ $\text{Li}_{0.90}\text{Ba}_{0.10}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
実施例8.	$\text{Li}_{1.18}\text{Ba}_{0.024}\text{Ni}_{0.800}\text{Mn}_{0.200}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.021}\text{Ni}_{0.80}\text{Mn}_{0.20}\text{O}_2$
実施例9.	$\text{Li}_{1.18}\text{Ba}_{0.024}\text{Ni}_{0.700}\text{Mn}_{0.300}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.021}\text{Ni}_{0.70}\text{Mn}_{0.30}\text{O}_2$
実施例10.	$\text{Li}_{1.03}\text{Ba}_{0.021}\text{Ni}_{0.900}\text{Co}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.020}\text{Ni}_{0.90}\text{Co}_{0.10}\text{O}_2$
実施例11.	$\text{Li}_{1.09}\text{Ba}_{0.021}\text{Ni}_{0.900}\text{Ti}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.019}\text{Ni}_{0.90}\text{Ti}_{0.10}\text{O}_2$
実施例12.	$\text{Li}_{1.03}\text{Ba}_{0.021}\text{Ni}_{0.900}\text{Cu}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.020}\text{Ni}_{0.90}\text{Cu}_{0.10}\text{O}_2$
実施例13.	$\text{Li}_{1.08}\text{Mg}_{0.022}\text{Ni}_{0.900}\text{Co}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Mg}_{0.021}\text{Ni}_{0.90}\text{Co}_{0.10}\text{O}_2$
実施例14.	$\text{Li}_{1.08}\text{Sr}_{0.022}\text{Ni}_{0.900}\text{Co}_{0.100}\text{O}_2$ $\text{Li}_{0.98}\text{Sr}_{0.020}\text{Ni}_{0.90}\text{Co}_{0.10}\text{O}_2$
実施例15.	$\text{Li}_{1.10}\text{Ni}_{0.900}\text{Mn}_{0.050}\text{Co}_{0.050}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{0.90}\text{Mn}_{0.051}\text{Co}_{0.049}\text{O}_2$
実施例16.	$\text{Li}_{1.10}\text{Ni}_{0.800}\text{Mn}_{0.100}\text{Co}_{0.100}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{0.80}\text{Mn}_{0.10}\text{Co}_{0.10}\text{O}_2$
実施例17.	$\text{Li}_{1.10}\text{Ni}_{0.700}\text{Mn}_{0.100}\text{Co}_{0.200}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{0.70}\text{Mn}_{0.10}\text{Co}_{0.20}\text{O}_2$
実施例18.	$\text{Li}_{1.10}\text{Ni}_{0.600}\text{Mn}_{0.100}\text{Cu}_{0.100}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{0.60}\text{Mn}_{0.10}\text{Cu}_{0.10}\text{O}_2$

Upper : Synthesis ratio

Lower : Measured by ICP

[Table 2]

Initial Capacity

表 2. 実施例の初期容量と容量保持率

	初期容量 (mAh/g)	容量保持率 (%)		初期容量 (mAh/g)	容量保持率 (%)
実施例 1	1 3 5	8 8	実施例11	1 4 4	9 4
実施例 2	1 3 8	9 0	実施例12	1 4 2	9 2
実施例 3	1 3 5	8 5	実施例13	1 4 0	9 2
実施例 4	1 3 5	8 2	実施例14	1 4 8	9 5
実施例 5	1 4 0	9 4	実施例15	1 3 8	9 0
実施例 6	1 3 8	8 7	実施例16	1 3 8	8 8
実施例 7	1 3 0	8 5	実施例17	1 3 5	8 6
実施例 8	1 3 8	9 3	実施例18	1 3 5	9 2
実施例 9	1 3 5	8 5	実施例19	1 4 0	9 4
実施例10	1 4 4	9 5			

Efficiency = Capacity @ 100th cycle / Capacity @ 1st cycle *100

[0036]

The Example of comparison

[Table 4]

表 4. 比較例の仕込み組成と定量分析組成

	上段：仕込み組成／下段：定量分析組成
比較例 1	$\text{Li}_{1.08}\text{Ni}_{1.00}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{1.0}\text{O}_2$
比較例 2.	$\text{Li}_{0.88}\text{Ba}_{0.22}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$ $\text{Li}_{0.80}\text{Ba}_{0.20}\text{Ni}_{0.90}\text{Mn}_{0.10}\text{O}_2$
比較例 3.	$\text{Li}_{1.08}\text{Ba}_{0.022}\text{Ni}_{0.60}\text{Mn}_{0.40}\text{O}_2$ $\text{Li}_{0.98}\text{Ba}_{0.020}\text{Ni}_{0.60}\text{Mn}_{0.40}\text{O}_2$
比較例 4.	$\text{Li}_{1.10}\text{Ni}_{0.60}\text{Mn}_{0.10}\text{Co}_{0.10}\text{O}_2$ $\text{Li}_{1.0}\text{Ni}_{0.60}\text{Mn}_{0.10}\text{Co}_{0.10}\text{O}_2$
比較例 5.	$\text{Li}_{0.98}\text{Ba}_{0.020}\text{Ni}_{0.80}\text{Mn}_{0.20}\text{O}_2$ $\text{Li}_{0.89}\text{Ba}_{0.017}\text{Ni}_{0.80}\text{Mn}_{0.20}\text{O}_2$
比較例 6.	$\text{Li}_{1.18}\text{Ba}_{0.024}\text{Ni}_{0.80}\text{Mn}_{0.20}\text{O}_2$ $\text{Li}_{1.1}\text{Ba}_{0.023}\text{Ni}_{0.80}\text{Mn}_{0.20}\text{O}_2$

Washed to remove
excessive alkalinity

[Table 3]

表 3. 比較例の初期容量と容量保持率

	初期容量 (mAh/g)	容量保持率 (%)
比較例 1	130	45
比較例 2	110	75
比較例 3	130	50
比較例 4	130	58
比較例 5	100	20
比較例 6	評価不能	評価不能
比較例 7	128	41